

# The promotion effect of catalytic activity by Ru substitution at the B site of $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y}\text{Ru}_y\text{O}_{3-z}$ for propane steam reforming

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**Abstract** A series of  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y}\text{Ru}_y\text{O}_{3-\delta}$  ( $0.1 \leq x \leq 0.5$ ,  $0.05 \leq y \leq 0.15$ ) materials was prepared by the sol–gel method to develop alternative catalysts for propane steam reforming. Catalyst characteristics were evaluated using physicochemical methods including X-ray diffraction, Brunauer–Emmett–Teller methods,  $\text{H}_2$  temperature-programmed reduction, and thermogravimetry analysis (TGA). Effects of the amount of ruthenium (Ru) and strontium and the steam-to-carbon ratio (S/C) were investigated. An increase in Ru content led to increased propane conversion and  $\text{H}_2$  yield, especially below 700 °C. Dramatic enhancement of catalytic activity was observed with  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$  under 600 °C, achieving propane conversion over 79% between 600 and 800 °C with maximum propane conversion and  $\text{H}_2$  yield of 98.3% and 63.3%, respectively. Also, good resistance to carbon formation for the  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$  catalyst was confirmed by long-term testing and TGA analysis.

**Keywords** Propane ·  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y}\text{Ru}_y\text{O}_3$  ·  $\text{H}_2$  · Steam reforming

## Introduction

Steam reforming (SR) of hydrocarbons is presently one of the least expensive hydrogen production methods. Recently, interest in SR of hydrocarbons has been

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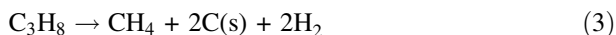
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increasing due to the need for efficient and cost-effective reforming technologies for hydrogen production as a future clean fuel for combustion engines and fuel cells [1].

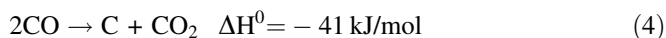
Liquefied petroleum gas (LPG), which contains mainly propane, is a promising alternative energy source for  $H_2$  production because it is easily transported and stored on-site and condenses at higher temperatures than natural gas [2]. Various processes have been studied for propane reforming, including partial oxidation, dry reforming, SR, and autothermal reforming. Of these processes, endothermic steam reforming has the main advantage of higher hydrogen content compared with other routes in which oxygen (air) is needed [3–6]. Steam reforming of propane is described by Eqs. 1 and 2.



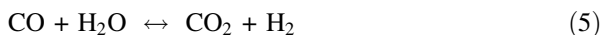
in which carbon deposition may occur via propane dehydrogenation (Eq. 3)



or the Boudouard reaction (Eq. 4)



with the possibility of the water gas shift reaction (WGS), Eq. 5.



Usually, supported Ni catalysts used in reforming of hydrocarbons are prepared by wet impregnation using various support materials. However, this method has the drawbacks of nonreproducibility and inhomogeneity of metal distribution on the support surface, and also fine metal particles tend to sinter at higher temperatures, resulting in catalyst deactivation. Furthermore, these catalysts are easily deactivated by coke deposition on the surface during reactions. Consequently, to overcome these problems, novel preparation and promotion techniques that can resist rapid catalyst deactivation from coking and sintering are essential [7–10].

Compared with Ni, ruthenium (Ru) has high SR activity, carbon deposition resistance, and sintering resistance. Suzuki et al. have tested Ru/ZrO<sub>2</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> cermet under solid oxide fuel cell (SOFC) anode operational conditions [11].

A class of materials known to have considerable catalytic activity is based on the perovskite oxide structure [12] of general formula ABO<sub>3</sub>, where the A sites may be occupied by rare-earth, alkaline-earth, alkali, or other large ions, and the B sites are usually filled with transition-metal cations. Moreover, the perovskite composition can be widely modified by partial replacement of A and/or B cations with other metals. The high stability of the perovskite structure allows this partial substitution and the consequent creation of structural defects such as anionic or cationic vacancies and/or change in the oxidation state of the transition-metal cation to maintain the electroneutrality of the compound. One interesting feature of these complex mixed oxides is that their catalytic activity can be greatly improved by partial substitution of the A and/or B sites, with only minor changes to the parent structure [13–17].

The aim of this study is to investigate novel catalysts for propane SR obtained by incorporation of Ru into the  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y}\text{Ru}_y\text{O}_{3-z}$  perovskite structure. Samples were prepared by a modified sol–gel method, and catalytic activity was determined by gas chromatography (GC). The catalysts were characterized by Brunauer–Emmett–Teller methods (BET), X-ray diffraction (XRD), and temperature-programmed reduction (TPR). Carbon formation after reactions was analyzed by thermogravimetry analysis (TGA).

## Experimental

### Catalyst preparation

All of the samples were prepared by a modified sol–gel method. Citric acid and ethylenediamine tetraacetic acid (EDTA) were used as complexing agents. Calculated amounts of La ( $\text{NO}_3$ )<sub>3</sub>·6H<sub>2</sub>O (GFS Chemicals),  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Sigma-Aldrich, 99%), and  $\text{Ru}(\text{NO})(\text{NO}_3)_3$  (Alfa) were used as precursors. A stoichiometric amount of nitrate was dissolved in distilled water, and the appropriate amounts of citric acid and EDTA (Sigma-Aldrich, 99%) were introduced into the solution at molar ratio of EDTA: citric acid: total metal ions of 1:1.5:1. The pH was adjusted to 9 with the addition of ammonia solution (20%, v/v). A gel formed after continuous heating (~65 °C) and stirring. The obtained gel was dried at room temperature for about 1 day. The dried gel was pretreated at 300 °C for 30 min and finally calcined at 1,000 °C for 5 h under ambient air.

### Characterization of catalysts

X-ray diffraction patterns were recorded on a DMAX-2500 (Rigaku) device using a Cu K<sub>α</sub> radiation source over a  $2\theta$  range from 20° to 80° in 0.05° steps. Comparison of the observed results with the JCPDS database was used to identify the catalyst phases.

The BET surface areas of catalysts were measured by N<sub>2</sub> physisorption using an ASAP 2020 (Micromeritics). Prior to analysis, samples were degassed at 150 °C for 2 h. BET results for the synthesized catalysts are presented in Table 1.

Temperature-programmed reduction (TPR) analyses were performed in an AutoChem 2920 (Micromeritics) equipped with a thermal conductivity detector

**Table 1** BET surface area results for  $\text{La}_x\text{Sr}_{1-x}\text{Cr}_{1-y}\text{Ru}_y\text{O}_3$  catalysts

Catalyst	BET surface area (m <sup>2</sup> g <sup>-1</sup> )
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.95}\text{Ru}_{0.05}\text{O}_3$	4.3
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.9}\text{Ru}_{0.1}\text{O}_3$	5.2
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$	6.3
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$	4.5
$\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$	6.1
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$	4.6
$\text{La}_{0.5}\text{Sr}_{0.5}\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$	3.8

(TCD) to investigate the reduction properties of the catalysts. Prior to analyses, catalysts were pretreated in Ar at 120 °C for 1 h to remove both impurities and water from the catalyst surface. Next, a 10% H<sub>2</sub>/Ar gas mixture was passed through the sample at total flow rate of 50 mL min<sup>-1</sup>, and the temperature was raised from room temperature to 900 °C at a rate of 10 °C min<sup>-1</sup>. TGA analysis was conducted for carbon deposition from long-term experiments with a Q50 (TA instruments Inc.). To remove water, samples were pretreated at 110 °C for 20 min under oxygen, and the change in weight was recorded from 50 °C to 1,000 °C at ramping rate of 10 °C min<sup>-1</sup>.

### Catalytic activity

Catalytic activity measurements were carried out at atmospheric pressure using a quartz reactor (i.d. = 12 mm) heated by an electric furnace at gas hourly space velocity (GHSV) of 34,000 h<sup>-1</sup> and reaction temperatures ranging from 600 to 800 °C. The reaction temperature was monitored by a K-type thermocouple inserted into the reactor through a quartz tube. The reaction gas was introduced into the reactor with a properly calibrated mass flow controller (Brooks, 5850E), and evaporated water was fed by an isocratic pump (KD Scientific, KDS 100). The reaction stream mixture consisted of 5% C<sub>3</sub>H<sub>8</sub>, 25% H<sub>2</sub>O, and 70% N<sub>2</sub> when the ratio of steam-to-carbon (S/C) was 1.7 and 5% C<sub>3</sub>H<sub>8</sub>, 15% H<sub>2</sub>O, and 80% N<sub>2</sub> when the S/C was 1. The catalyst loading weight was 100 mg, and all experiments were carried out with total flow rate of 100 cm<sup>3</sup> min<sup>-1</sup>. Reaction products were analyzed by a gas chromatograph (Younglin, M600D) equipped with TCD and flame ionization detector (FID) detectors. Before the reaction, all of the catalysts were reduced under 10% H<sub>2</sub> in nitrogen at 800 °C for 1 h. Long-term stability investigation was carried out for chosen catalysts at 800 °C for 24 h. The propane conversion, H<sub>2</sub> yield, and CO and CO<sub>2</sub> selectivity were calculated with the following equations:

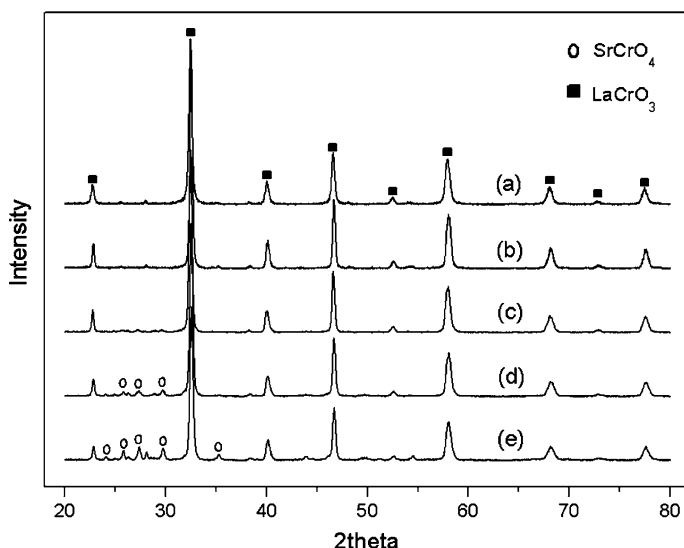
$$\text{C}_3\text{H}_8 \text{ conversion } (\%) = \frac{\text{moles of propane converted}}{\text{total moles of propane in feed}} \times 100$$

$$\text{H}_2 \text{ yield } (\%) = \frac{2 \times \text{moles of H}_2 \text{ produced}}{\text{total moles of hydrogen in feed}} \times 100$$

$$\text{Selectivity of CO, CO}_2, \text{CH}_4 (\%) = \frac{\text{moles of CO, CO}_2, \text{CH}_4}{3 \times \text{moles of propane converted}} \times 100$$

### Results and discussion

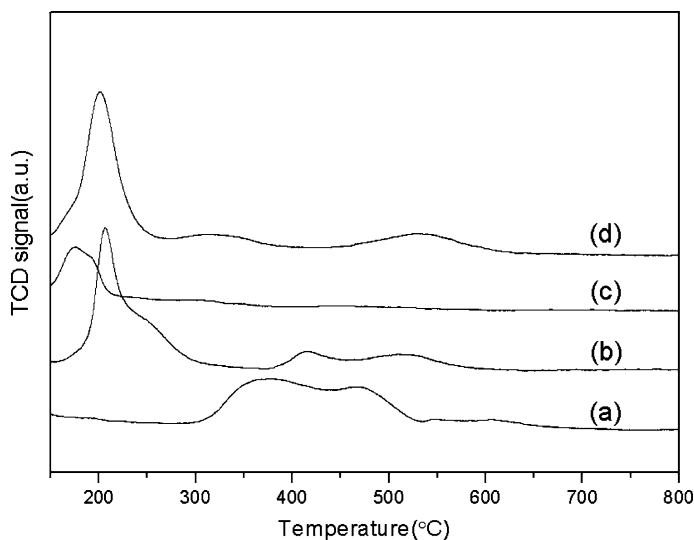
The XRD patterns of La<sub>1-x</sub>Sr<sub>x</sub>Cr<sub>0.85</sub>Ru<sub>0.15</sub>O<sub>3</sub> catalysts after calcination for 5 h at 1000 °C in air are shown in Fig. 1. All of the catalysts had the perovskite structure represented by diffraction lines at 22.83°, 32.55°, 46.68°, and 58.2° which originate from LaCrO<sub>3</sub> (JCPDS, 241016), and they crystallized with an orthorhombic unit cell, *a* = 5.479 Å, *b* = 5.513 Å, *c* = 7.756 Å. As shown in Fig. 1, no intermediate phase containing Ru was detected. A second phase of SrCrO<sub>4</sub> (JCPDS, 350743)



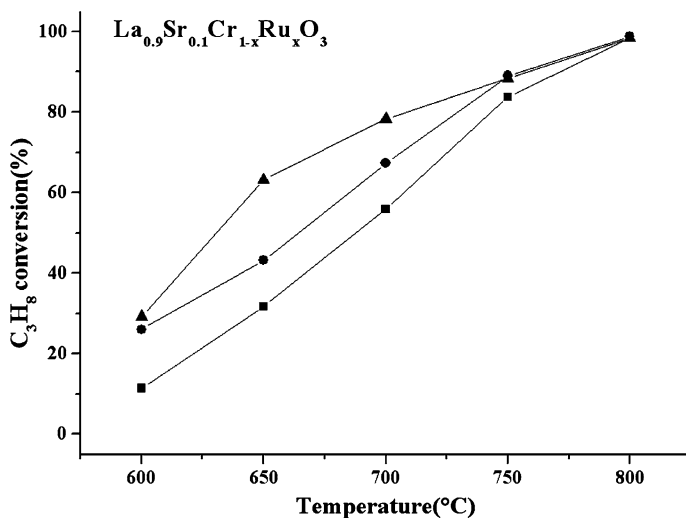
**Fig. 1** XRD patterns of  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$ : *a*  $x = 0.1$ , *b*  $x = 0.2$ , *c*  $x = 0.3$ , *d*  $x = 0.4$ , and *e*  $x = 0.5$ ; perovskite (filled squares),  $\text{SrCrO}_4$  (open circles)

which has monoclinic crystals was detected around  $24\text{--}30^\circ$  when  $x$  was more than 0.4. As reported by Vernoux et al. [18], the formation of  $\text{SrCrO}_4$  was detected for  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$  prepared by a spray pyrolysis method at  $1200^\circ\text{C}$ . The formation of a homogeneous crystal structure  $\text{LaCrO}_3$  for  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$  at  $x < 0.4$  could be a consequence of the sol–gel method. Ding et al. reported that the  $\text{SrCrO}_4$  phase finally decomposed and dissolved into the perovskite structure when the calcination temperature was increased to  $1350^\circ\text{C}$  [19]. The results of surface area measurements are presented in Table 1. Increasing the amount of Ru doping from 0.05 to 0.15 resulted in a slight increase of surface area from  $4.3$  to  $6.3\text{ m}^2\text{ g}^{-1}$ . An increase in the amount of strontium (Sr) doping at constant Ru doping gave a similar surface area for  $\text{La}_{0.5}\text{Sr}_{0.5}\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$  of  $3.8\text{ m}^2/\text{g}$ . This result might be due to the formation of another phase such as  $\text{SrCrO}_4$ .

The reducibility of catalysts after calcinations at  $1000^\circ\text{C}$  was characterized by  $\text{H}_2$  TPR. Figure 2 shows the TPR profiles of the  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{1-x}\text{Ru}_x\text{O}_3$  samples. When Ru was not incorporated into the Cr site, a broad peak from  $300$  to  $530^\circ\text{C}$  was observed. This peak could be attributable to reduction of Cr in the perovskite structure as reported by Yan et al. [20]. The broad peak suggests that the oxidation state of Cr is not constant because of Sr doping. This peak disappeared and a trace peak was observed after Ru doping, as shown in Fig. 2b–d, which suggests that the reducibility of Cr in perovskite was changed by Ru doping. Further investigation will be necessary to gain insight into this phenomenon. The reduction peak around  $200^\circ\text{C}$  after Ru doping could be ascribed to the reduction of the Ru species in perovskite. As the Ru content was increased, the peak area also increased. Hurst et al. suggested that, for Ru on different supports, the peak around  $200^\circ\text{C}$  is due to reduction of  $\text{Ru}^{3+}$  to  $\text{Ru}^{2+}$  species [21].

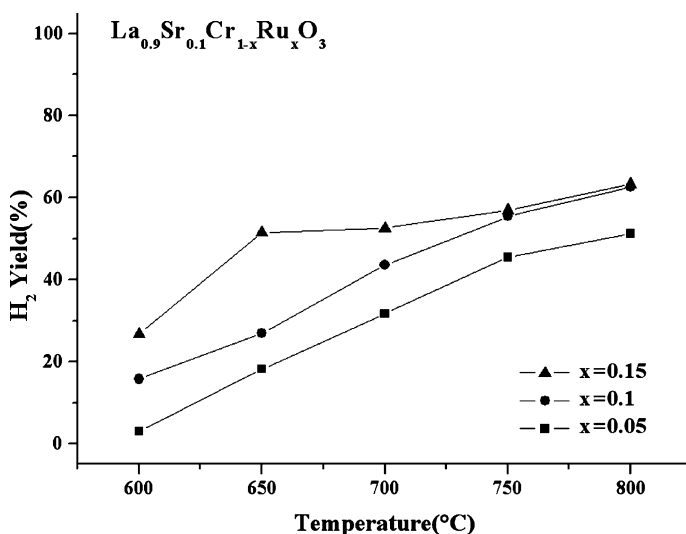


**Fig. 2** TPR profiles of  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{1-x}\text{Ru}_x\text{O}_3$ :  $a$   $x = 0$ ,  $b$   $x = 0.05$ ,  $c$   $x = 0.1$ , and  $d$   $x = 0.15$



**Fig. 3** Effect of Ru substitution in  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{1-x}\text{Ru}_x\text{O}_3$  on  $\text{C}_3\text{H}_8$  conversion at different reaction temperatures ( $\text{S/C} = 1.7$ ;  $\text{GHSV} = 34,000 \text{ h}^{-1}$ ):  $x = 0.05$  (filled squares),  $x = 0.1$  (filled circles), and  $x = 0.15$  (filled triangles)

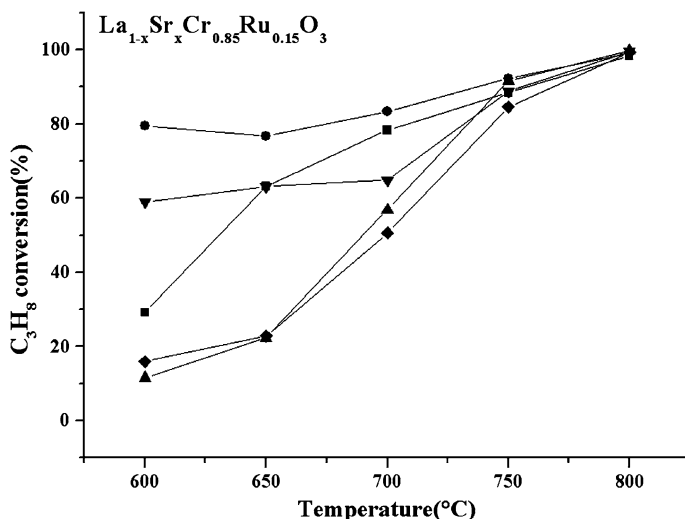
Figures 3 and 4 show the Ru substitution effect on propane conversion and  $\text{H}_2$  yield obtained with  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{1-x}\text{Ru}_x\text{O}_3$  catalysts. As Ru substitution was increased from 0.05 to 0.15, the propane conversion and  $\text{H}_2$  yield increased, especially below  $700^\circ\text{C}$ . The  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$  catalyst gave the best performance in terms of propane conversion and  $\text{H}_2$  yield over the reaction temperature range. At  $800^\circ\text{C}$ , a maximum propane conversion and  $\text{H}_2$  yield of



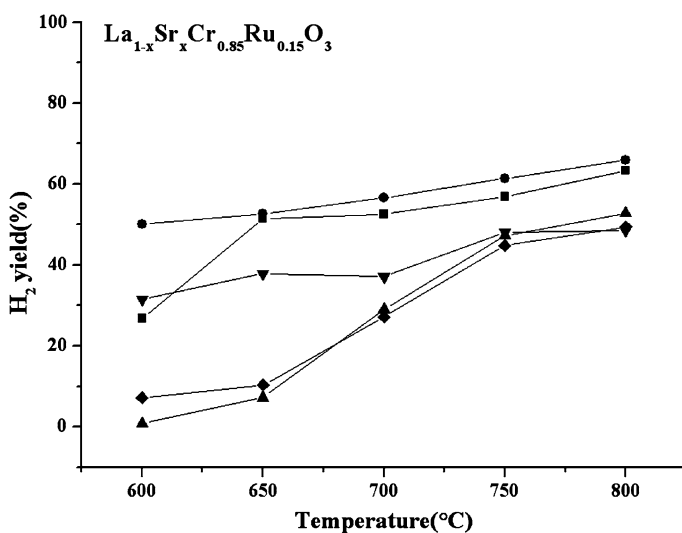
**Fig. 4** Effect of Ru substitution in  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{1-x}\text{Ru}_x\text{O}_3$  on  $\text{H}_2$  yield at different reaction temperatures ( $\text{S/C} = 1.7$ ;  $\text{GHSV} = 34,000 \text{ h}^{-1}$ ):  $x = 0.05$  (filled squares),  $x = 0.1$  (filled circles), and  $x = 0.15$  (filled triangles)

99.54% and 63.3%, respectively, were obtained. A slower increasing rate of  $\text{H}_2$  yield compared with propane conversion was observed, which suggests that the SR reaction was not the sole reaction. As reported by Rostrup-Nielsen and Alstrup [22], methanation and hydrogenolysis reactions occurred simultaneously, consuming the hydrogen formed in the steam reaction. Formation of  $\text{CH}_4$  was also detected during reactions conducted above 650 °C (data not shown).

Catalytic activity of  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$  catalysts as a function of Sr content is shown in Figs. 5 and 6. The highest propane conversion and  $\text{H}_2$  yield of 99.2% and 65.6%, respectively, were obtained with  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$ . No obvious correlation was observed for propane conversion and hydrogen yield with respect to Sr content. Propane conversion of 79.5% and  $\text{H}_2$  yield of 50% at 600 °C were observed with  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$ , which suggests that catalytic activity was greatly increased at lower temperature by slightly increasing the Sr doping from 0.1 to 0.2. A further increase in Sr doping did not increase catalyst activity at 600 °C. On the other hand, 10% conversion was observed with  $\text{La}_{0.5}\text{Sr}_{0.5}\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$ . A similar tendency was also seen for  $\text{H}_2$  yield. Hydrogen was not detected at 650 °C with  $\text{La}_{0.5}\text{Sr}_{0.5}\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$ , although the propane conversion was 10%. This result could be explained by propane decomposition to lighter hydrocarbon or carbon species without the reforming reaction occurring. The differences of propane conversion and  $\text{H}_2$  yield at the same temperature with respect to Sr doping content were quite large. Catalytic activity was affected more strongly by Sr doping than by Ru doping. However, relatively high conversion and  $\text{H}_2$  yield were obtained from Ru doping. Sauvet et al. [23] reported that Sr doping promotes Ru stabilization in the tetravalent state in the perovskite structure even during reaction processes, thus



**Fig. 5** Effect of Sr substitution in  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$  on  $\text{C}_3\text{H}_8$  conversion at different reaction temperatures ( $\text{S/C} = 1.7$ ;  $\text{GHSV} = 34,000 \text{ h}^{-1}$ ):  $x = 0.1$  (filled squares),  $x = 0.2$  (filled circles),  $x = 0.3$  (filled triangles),  $x = 0.4$  (filled inverted triangles), and  $x = 0.5$  (filled diamonds)

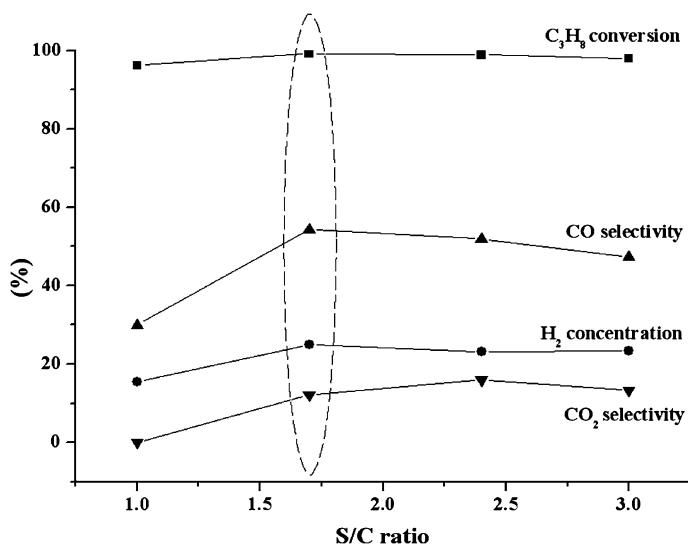


**Fig. 6** Effect of Sr substitution in  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$  on  $\text{H}_2$  yield at different reaction temperatures ( $\text{S/C} = 1.7$ ;  $\text{GHSV} = 34,000 \text{ h}^{-1}$ ):  $x = 0.1$  (filled squares),  $x = 0.2$  (filled circles),  $x = 0.3$  (filled triangles),  $x = 0.4$  (filled inverted triangles), and  $x = 0.5$  (filled diamonds)

Sr doping of the perovskite structure appears to play an important role in catalyst activity.

To evaluate the effect of the  $\text{S/C}$  ratio on catalytic activity, the  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$  catalyst was used. All experiments were conducted with  $\text{S/C} = 1, 1.7$ , and

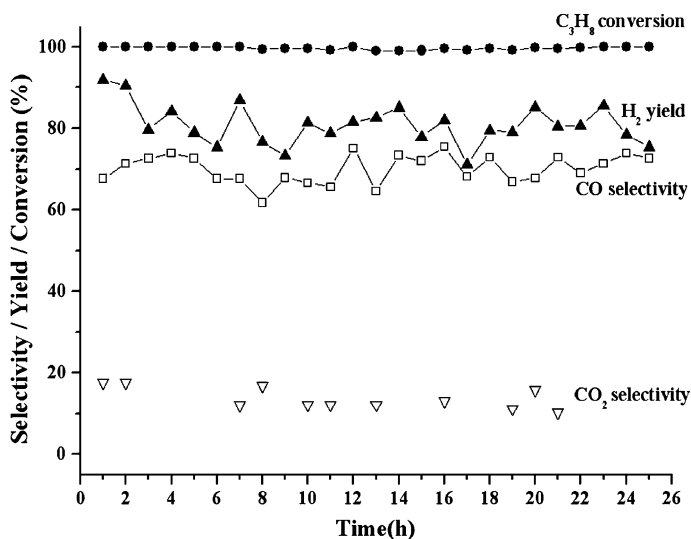




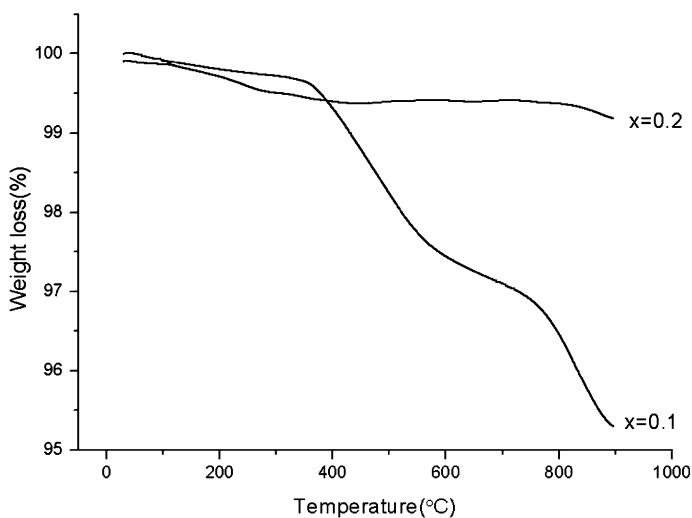
**Fig. 7** Change in H<sub>2</sub> composition as a function of La<sub>0.8</sub>Sr<sub>0.2</sub>Cr<sub>0.85</sub>Ru<sub>0.15</sub>O<sub>3</sub> catalyst S/C ratio (GHSV = 34,000 h<sup>-1</sup>; temperature = 800 °C)

3 at 800 °C. Theoretically, the stoichiometry of propane and steam for SR to produce hydrogen and CO is 1:3, which is equivalent to S/C of 1. However, according to Le Chatelier's principle, it would be expected that propane conversion and H<sub>2</sub> yield would improve as the S/C ratio was increased. As shown in Fig. 8, a slight increase of H<sub>2</sub> concentration was observed. Some researchers have reported that no significant increase was obtained with a S/C ratio increase [6, 24], the same trend as observed in our study. As shown in Fig. 7, small increases of propane conversion and H<sub>2</sub> yield were observed as the S/C was increased from 1 to 1.7. A further increase of S/C did not increase either the propane conversion or the H<sub>2</sub> concentration.

To evaluate the deactivation behavior of catalysts, long-term tests were conducted using La<sub>0.9</sub>Sr<sub>0.1</sub>Cr<sub>0.85</sub>Ru<sub>0.15</sub>O<sub>3</sub> at 800 °C with S/C ratio of 1.7 over 24 h. As shown in Fig. 8, propane conversion remained approximately 96% and H<sub>2</sub> yield was maintained above approximately 70%, with small variations observed during the reaction. In Fig. 9, the TGA profiles of La<sub>0.9</sub>Sr<sub>0.1</sub>Cr<sub>0.85</sub>Ru<sub>0.15</sub>O<sub>3</sub> and La<sub>0.8</sub>Sr<sub>0.2</sub>Cr<sub>0.85</sub>Ru<sub>0.15</sub>O<sub>3</sub> after long-term experiments are shown. The percentage weight loss of the samples was 4.2% and 0.8% for La<sub>0.9</sub>Sr<sub>0.1</sub>Cr<sub>0.85</sub>Ru<sub>0.15</sub>O<sub>3</sub> and La<sub>0.8</sub>Sr<sub>0.2</sub>Cr<sub>0.85</sub>Ru<sub>0.15</sub>O<sub>3</sub>, respectively. From these results, the La<sub>0.8</sub>Sr<sub>0.2</sub>Cr<sub>0.85</sub>Ru<sub>0.15</sub>O<sub>3</sub> catalyst was more resistant to carbon deposition during propane steam reforming than La<sub>0.9</sub>Sr<sub>0.1</sub>Cr<sub>0.85</sub>Ru<sub>0.15</sub>O<sub>3</sub>. Since a decrease of propane conversion during long-term testing was not observed for either catalyst, the carbon species deposited on the catalysts did not have an influence on catalytic activity. Similar results have been reported by Trimm [25].



**Fig. 8** Change in catalytic activity of  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$  catalyst as a function of reaction time ( $\text{S/C} = 1.7$ ;  $\text{GHSV} = 34,000 \text{ h}^{-1}$ , temperature =  $800^\circ\text{C}$ )  $\text{C}_3\text{H}_8$  conversion (filled circles),  $\text{H}_2$  yield (filled triangles),  $\text{CO}$  selectivity (open squares),  $\text{CO}_2$  selectivity (open inverted triangles)



**Fig. 9** Thermogravimetric curves of  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$  after long-term stability testing ( $\text{S/C} = 1.7$ ;  $\text{GHSV} = 34,000 \text{ h}^{-1}$ ; temperature =  $800^\circ\text{C}$ )

## Conclusions

In this study, Sr- and Ru-substituted  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y}\text{Ru}_y\text{O}_{3-\delta}$  ( $0.1 \leq x \leq 0.5$ ,  $0.05 \leq y \leq 0.15$ ) catalysts were prepared in the presence of citric acid and EDTA

using the sol–gel method. The effects of Sr and Ru substitution on catalytic activity in SR of propane were investigated. The following conclusions can be drawn from the results of both the activity tests and catalyst characterization:

1. A perovskite structure of the  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_{3-\delta}$  catalysts was confirmed after calcinations at 1000 °C by X-ray diffraction, but a second  $\text{SrCrO}_4$  phase was detected as the Sr substitution increased over  $x = 0.4$ .
2. The highest catalytic activity was observed for  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$ , achieving propane conversion and  $\text{H}_2$  yield of 98.3% and 63.3% at 800 °C. With an increase in the amount of Ru substitution, propane conversion increased over the reaction temperature range, with a distinct improvement in propane conversion observed at 650 °C. At 600 °C, catalytic activity was greatly increased by 20% on replacement of La with Sr, achieving propane conversion of about 80%. However, a clear correlation between Sr doping and catalytic activity was not determined. An increase of S/C had less of an effect on catalytic activity than did Ru or Sr doping. Although a small amount of carbon deposition was observed in the long-term tests, catalytic activity was not affected. Higher carbon resistance was observed for the  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$  catalyst by TGA analysis.

From these results, the most suitable catalyst for propane steam reforming was found to be  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$ .

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